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Niobium nanoclusters studied with *in situ* transmission electron microscopy

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Structural aspects of deposited niobium nanoclusters approximately 10 nm in size have been explored by means of high-resolution transmission electron microscopy. The niobium clusters have a bcc structure and a crystal habit of rhombic dodecahedron. *In situ* heating up to $\sim 800^\circ\text{C}$ revealed a resistance to high temperatures, in the sense that the cluster habit is preserved. However, the internal structural order of the clusters is altered due to formation of niobium oxide domains within the clusters. Coalescence does not occur even at the highest temperatures, which is attributed to the presence of facets and the occurrence of oxidation during heat treatment. © 2003 American Institute of Physics. [DOI: 10.1063/1.1625789]

Nanostructured materials are widely studied because of their potential in advanced materials and devices. The study of nanocluster assembled thin layers is driven by two major technological reasons.^{1–11} The first stems from the demand to miniaturize further microelectronic devices where one would like to grow well-organized nanometer-size islands with specific electronic properties. The second reason finds its origin in tailoring nanostructured materials for specific functional properties that differ from their bulk counterparts.

Transition metal clusters, mostly those of Fe, Co, Ni, and Nb, have been the subject to a large number of studies dealing with their structure, chemical reactivity, magnetic properties, and ionization potentials.⁸ Nb is a nonmagnetic transition metal, offering relative simplicity in the relationship between structure and functional cluster properties. Nb atoms form strong directional chemical bonds, which lead to well-defined structures.⁸ The majority of studies on Nb clusters thus far have focused on systems with a rather small number of atoms per cluster (<30), and their special physical properties (ionization potential, electron affinity, atomization energy as a function of cluster size),⁹ as well as structural properties.¹⁰ Research on the *dynamical* aspects of larger size niobium clusters as a function of temperature has been very limited. It has been suggested that Nb nanoparticles possess a crystal habit that is a truncated rhombic dodecahedron.¹¹ Nevertheless, our high-resolution transmission electron microscopy (HRTEM) investigations show another possibility, as will be explained in this letter. Therefore, in this work we explore the crystallography of nanometer scale Nb clusters, in addition to any cluster-cluster interactions and structural transitions that might occur under *in situ* heat treatment up to a temperature of 800°C .

Cluster deposition was performed using a NC200U source manufactured by Oxford Applied Research.² It is based on the gas aggregation technique,² using a magnetron sputtering device to create a vapor of Nb atoms. These atoms then aggregate in a flow of Ar gas (pressure 2×10^{-3} mbar) forming clusters. The chamber base pressure was $\sim 10^{-9}$

mbar. The magnetron power was set to 100 W with a plasma current of about 0.5 A. Clusters were deposited directly onto silicon nitride and carbon support films of thickness 20 nm for analysis in a JEOL 2010F transmission electron microscope (TEM). The samples were briefly exposed to air during transfer to the microscope.

An advantage of the source is that it provides a relatively monodisperse cluster size with an average cluster diameter of 10 nm (see Fig. 1). The Nb nanoclusters are randomly deposited [Fig. 1(a)], where any self-arrangement on a two-dimensional (2D) superlattice is excluded. Deposition occurred at room temperature, and at low energy to ensure that the Nb clusters remained intact having a bcc structure as diffraction analysis indicated [Fig. 1(b)].

Figure 2 depicts high-resolution TEM images of (a) as-

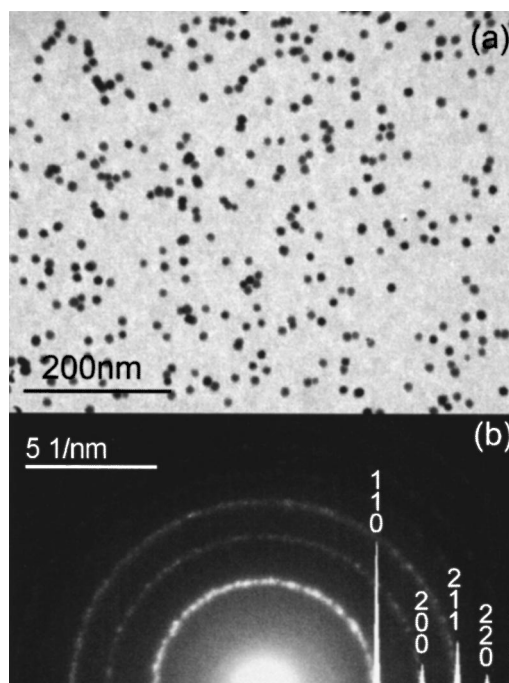


FIG. 1. (a) TEM bright-field image showing random distribution of as-deposited Nb nanoclusters, (b) selected area diffraction of the as-deposited film; the simulation of the diffraction profile for bcc niobium is superimposed.

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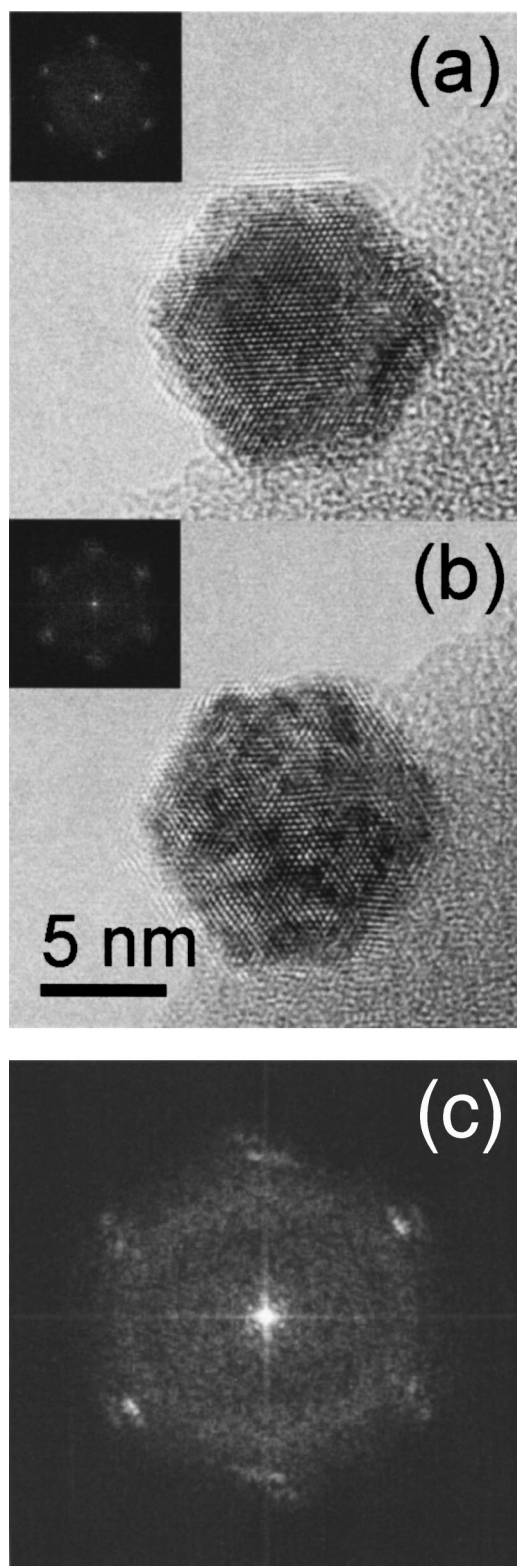


FIG. 2. (a) A single Nb nanocluster as-deposited on a Si_3N_4 membrane, (b) the same cluster after heat treatment at 700 °C. The upper insets in both images represent the corresponding power spectra, (c) magnified power spectrum of the heat-treated cluster where is shown the clear appearance of the radial and the circumferential spot splitting.

deposited which represents $\langle 111 \rangle_{\text{bcc}}$ projection and (b) annealed single Nb cluster. No oxide shell is detectable as in our previous case of iron clusters.¹² Deposited clusters do not exhibit structural instabilities or collapsing under electron beam irradiation. The temperature of 800 °C is the highest that the Si_3N_4 substrate can withstand. Considerable struc-

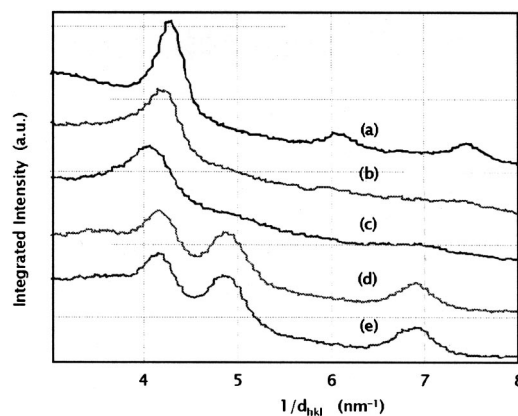


FIG. 3. The top schematic shows Integrated intensity of the diffraction peaks in range of 3–8.5 nm^{-1} as it develops during *in situ* heat treatment: (a) as-deposited, (b) 300, (c) 500, (d) 800 °C, (e) cooled slowly back to RT. First, the shift and broadening of the peak is visible, then, the fcc structure appears remaining unaltered upon cooling to RT.

tural changes occur as a result of the heat treatment as is shown in diffraction analysis (Fig. 3). The first structural changes are detectable at 300 °C by the slight shift of the 110 peak. The maximum shift is observed at 500 °C, where the shift represents an expansion of the lattice parameter approximately by 7%, which is at the initial stage of the bcc to fcc structural transformation (Fig. 3). The structural changes are due to oxidation of the clusters with the NbO (cubic monoxide) to be the most possible structure, since it is known to form under low oxygen pressures.¹³ This is typical for the ambient vacuum of $\sim 10^{-7}$ Torr during *in situ* heat treatment inside the TEM. In addition, the electron energy loss spectroscopy performed after annealing shows clear presence of the oxygen in analyzed area, undoubtedly confirming the formation of the niobium oxide.

More detailed information is provided by lattice imaging on Fig. 2(b), which corresponds to the cluster displayed in Fig. 2(a) after a heat treatment at 800 °C. Splitting and shifting of the originally 110_{bcc} spots is visible in the inset of Fig. 2(b) representing its power spectra. Measured proportion of the split spots corresponds to the value 1.145, which is in good agreement with the theoretical value for fcc lattice $d_{111}/d_{200}=1.155$. These observations point to the formation of niobium oxide subdomains of various 110 orientations within the nanocluster. The latter exclude the formation of niobium monoxide monocrystal of $\langle 110 \rangle_{\text{fcc}}$ orientation. The heat treated structure remains unaltered upon slowly cooling down to room temperature.

In general the crystal structure and habit of nanoparticles depend on temperature and composition. In many cases the particles have a polyhedral form with various degrees of truncation. These shapes occur since they lead to surface energy minimization for particles formed at equilibrium, or because of kinetics where the shape is determined by the rate at which different crystal faces grow. The combination of factors such as temperature, kinetics, impurities, and surface energy effects could lead also to unusual nanoparticle shapes and size distributions.¹¹

The crystal structure at room temperature as is shown by the $\langle 111 \rangle$ projection having a hexagonal shape corresponds to a rhombic dodecahedron, while a hexagonal $\langle 110 \rangle$ and a

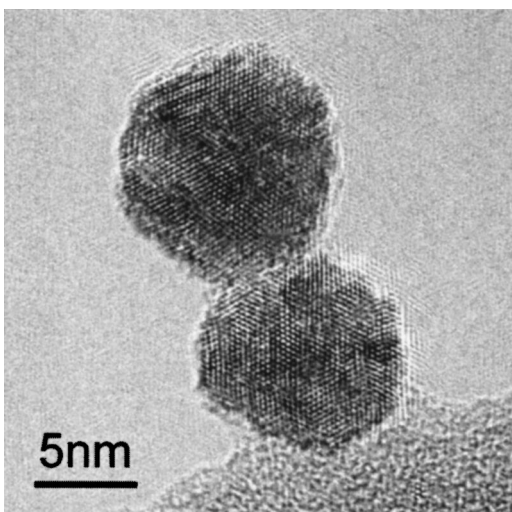


FIG. 4. Two Nb nanoclusters after heat treatment at 700 °C; no coalescence is observed.

square $\langle 100 \rangle$ projections were also found. Truncation of the rhombic dodecahedron increases the spherical shape of the cluster, while also increasing the fraction of the energetically less favorable faces. The degree of truncation can be described by the ratio R_{TR} , which is given by $R_{TR} = 2 - 2/\sqrt{2}(\gamma_{100}/\gamma_{110})$ ¹² based on the Wulff construction. When $R_{TR}=0$ there is no truncation of the rhombic dodecahedron, while when $R_{TR}=1$ we have a fully truncated shape, i.e., a cuboctahedron. Therefore, the case of untruncated dodecahedron ($R_{TR}=0$) yields a ratio of surface energies ($\gamma_{100}/\gamma_{110} \geq \sqrt{2}$) is in agreement with the fact that the $\{110\}$ faces have the lowest surface energy for bcc structures.¹⁴

Figure 4 illustrates that cluster coalescence events were not observed even at rather elevated temperatures of $T \cong T_M/3$ (with $T_M=2750$ K and $T_M=2210$ K the melting temperatures of bulk Nb and NbO, respectively),¹⁵ although the melting temperature of clusters will be lower than T_M due to its dependence on cluster diameter.^{16,17} The driving force for coalescence is the diffusion of atoms on the cluster surface from the regions of high curvature (where they have fewer neighbors and therefore are less strongly bound) towards the regions of lower curvature. The absence of coalescence supports the hypothesis that the cluster melting temperature is close to the bulk value. Long coalescence times have also been attributed to the presence of facets (as in Fig. 2) on the initial cluster surface, that persist and rearrange during coalescence.^{4,18}

Indeed, for faceted nanosize clusters, diffusion of surface atoms has been observed to be slow even at temperatures 200° below the melting point, allowing thus very few atoms to move a significant distance away from the contact region.⁴ Experiments have shown that shape evolution is very slow in the presence of facets for three-dimensional crystallites.⁴ Both experiments¹⁹ and computer simulations⁴ on 2D islands suggest that the presence of facets can be effective in slowing down the coalescence process. More work is underway to get a quantitative understanding of nanoparticle coalescence by including crystalline anisotropy in the surface diffusion theory of Mullins and Nichols.^{20,21}

If we compare Nb to Fe nanoclusters (both corresponding to a bcc system) prepared with the same source under

identical conditions,¹² the as-deposited Fe clusters were enclosed by an oxide shell of thickness ~ 2 nm while for Nb any oxide shell is rather undetectable with oxidation occurring upon further heat treatments at elevated temperatures. Indeed, upon a heat treatment up to temperatures as high as $T_m/3$, the Fe cluster coalescence was fast with the clusters fully fused into larger ones. After disintegration of the oxide, the crystal habit of the annealed Fe nanoclusters was a truncated rhombic dodecahedron.¹² We should also point out that in Fig. 2 we do not observe any significant change in cluster size after heat treatment. Indeed, even if the whole cluster was oxidized forming NbO, since for the Nb and NbO the volume per atom is $1.808 \times 10^{-2} \text{ nm}^3$ and $2.541 \times 10^{-2} \text{ nm}^3$,¹³ respectively, that would lead to a size ratio $d_{\text{NbO}}/d_{\text{Nb}} \approx 1.12$. The latter yields an increment in size at most by 12%, which could be observed by HRTEM. However, the presence of the delocalization effect around the cluster edges can hinder such a small size increments of the order of 10%.

In conclusion, cluster coalescence is negligible even up to 800 °C, which indicates that there is no diffusion of surface atoms to drive coalescence. A significant role is played by the presence of facets that generally suppress the tendency to coalesce, and the presence of the niobium oxide phase.

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